













**METHOD FOR PRODUCING A HIGH STRENGTH Al-Zn-Mg-Cu ALLOY****Publication number:** WO2004001080**Publication date:** 2003-12-31**Inventor:** BENEDICTUS RINZE (NL); HEINZ ALFRED LUDWIG (DE); KEIDEL CHRISTIAN JOACHIM (DE)**Applicant:** CORUS ALUMINIUM WALZPROD GMBH (DE); BENEDICTUS RINZE (NL); HEINZ ALFRED LUDWIG (DE); KEIDEL CHRISTIAN JOACHIM (DE)**Classification:****- international:** **C22C21/10; C22F1/053; C22C21/10; C22F1/053;**  
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The present invention relates to a method for producing a high strength Al-Zn-Cu-Mg alloy with an improved fatigue crack growth resistance and a high damage tolerance, comprising the steps of casting an ingot with the following composition (in weight percent) Zn 5.5- 9.5, Cu 1.5 - 3.5, Mg 1.5 - 3.5, Mn < 0.25, Zr < 0.25, Cr < 0.10, Fe < 0.25, Si < 0.25, Ti < 0.10, Hf and/or V < 0.25, other elements each less than 0.05 and less than 0.15 in total, balance aluminium, homogenising and/or pre-heating the ingot after casting, hot working the ingot and optionally cold working into a worked product of more than 50 mm thickness, solution heat treating, quenching the heat treated product, and artificially aging the worked and heat-treated product, wherein the aging step comprises a first heat treatment at a temperature in a range of 105 DEG C to 135 DEG C for more than 2 hours and less than 8 hours and a second heat treatment at a higher temperature than 135 DEG C but below 170 DEG C for more than 5 hours and less than 15 hours. The product achieved by the method exhibits a compression yield strength of at least 510 Mpa and an ST elongation at S/2 of at least 3.0 %. The invention concerns a weldable plate product of such high strength Al-Zn-Cu-Mg having a thickness of more than 50 mm and an aircraft structural member produced from such alloy.

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(54) Title: METHOD FOR PRODUCING A HIGH STRENGTH Al-Zn-Mg-Cu ALLOY

(57) **Abstract:** The present invention relates to a method for producing a high strength Al-Zn-Cu-Mg alloy with an improved fatigue crack growth resistance and a high damage tolerance, comprising the steps of casting an ingot with the following composition (in weight percent) Zn 5.5- 9.5, Cu 1.5 - 3.5, Mg 1.5 - 3.5, Mn < 0.25, Zr < 0.25, Cr < 0.10, Fe < 0.25, Si < 0.25, Ti < 0.10, Hf and/or V < 0.25, other elements each less than 0.05 and less than 0.15 in total, balance aluminium, homogenising and/or pre-heating the ingot after casting, hot working the ingot and optionally cold working into a worked product of more than 50 mm thickness, solution heat treating, quenching the heat treated product, and artificially aging the worked and heat-treated product, wherein the aging step comprises a first heat treatment at a temperature in a range of 105°C to 135°C for more than 2 hours and less than 8 hours and a second heat treatment at a higher temperature than 135°C but below 170°C for more than 5 hours and less than 15 hours. The product achieved by the method exhibits a compression yield strength of at least 510 Mpa and an ST elongation at S/2 of at least 3.0 %. The invention concerns a weldable plate product of such high strength Al-Zn-Cu-Mg having a thickness of more than 50 mm and an aircraft structural member produced from such alloy.



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**METHOD FOR PRODUCING A HIGH STRENGTH Al-Zn-Mg-Cu ALLOY**

The present invention relates to a method for producing a high strength Al-Zn-Cu-Mg alloy with an improved corrosion resistance while at the same time maintaining a high damage tolerance, a plate product of a high strength Al-Zn-Cu-Mg alloy produced in accordance with the inventive method having a thickness of more than 50 mm and an aircraft structural member produced from such alloy. More specifically, the present invention relates to a high strength Al-Zn-Cu-Mg alloy designated by the 7000-series of the international nomenclature of the Aluminium Association for structural aeronautical applications. Even more specifically, the present invention relates to a thick aluminium alloy product having improved combinations of strength, toughness and corrosion resistance, particularly a good strength-corrosion balance.

It is known in the art to use heat treatable aluminium alloys in a number of applications involving relatively high strength, high toughness and corrosion resistance such as aircraft fuselages, vehicular members and other applications. Aluminium alloys AA7050 and AA7150 exhibit high strength in T6-type tempers, see for example US-6,315,842. Also precipitation-hardened AA7x75 alloy products exhibit high strength values in the T6 temper. The T6 temper is known to enhance the strength of the alloy, wherein the aforementioned AA7050, AA7x50 and AA7x75 alloy products which contain high amounts of zinc, copper and magnesium are known for their high strength-to-weight ratios and, therefore, find application in particular in the aircraft industry. However, these applications result in exposure to a wide variety of climatic conditions necessitating careful control of working and ageing conditions to provide adequate strength and resistance to corrosion, including both stress corrosion and exfoliation.

In order to enhance resistance against stress corrosion and exfoliation as well as fracture toughness it is known to artificially over-ageing these 7000-series alloys. When artificially aged to a T79, T76, T74 or T73-type temper their resistance to stress corrosion, exfoliation corrosion and fracture toughness improve in the order stated (T73 being best and T79 being close to T6) but at some cost to strength compared to the T6 temper condition. An acceptable temper condition is the T74-type temper which is a limited over-aged condition, between T73 and T76, in order to obtain an acceptable level of tensile strength, stress corrosion resistance, exfoliation corrosion resistance and fracture toughness. Such a T74 temper is performed by over-ageing the aluminium alloy product at temperatures of 121°C for 6 to 24 hours and 171°C for about 14 hours.

Depending on the design criteria for a particular airplane component even small improvements in strength, toughness or corrosion resistance result in weight savings, which translate to fuel economy over the life time of the aircraft. To meet these demands several other AA7000-series alloys have been developed.

5 US Patent No. 4,954,188 discloses a method for providing a high strength aluminium alloy characterised by improved resistance to exfoliation using an alloy consisting of the following alloying elements, in wt. %:

Zn: 5.9 - 8.2  
Cu: 1.5 - 3.0  
10 Mg: 1.5 - 4.0  
Cr: < 0.04,

other elements such as zirconium, manganese, iron, silicon and titanium in total less than 0.5, the balance aluminium, working the alloy into a product of a pre-determined shape, solution heat treating reshaped product, quenching, and ageing the heat  
15 treated and quenched product to a temperature of from 132°C to 140°C for a period of from 6 to 30 hours. The desired properties of having high strength, high toughness and high corrosion resistance were achieved in this alloy by lowering the ageing temperature rather than raising the temperature as taught previously from e.g. US patent No. 3,881,966 or US Patent No. 3,794,531.

20 It has been reported that the known precipitation-hardened aluminium alloys AA7075 and other AA7000-series alloys, in the T6 temper condition, have not given sufficient resistance to corrosion under certain conditions. The T7-type tempers which improve the resistance of the alloys to stress-corrosion cracking, however, decrease strength significantly *vis-à-vis* the T6 condition.

25 US Patent No. 4,863,528 therefore discloses a method for producing an improved aluminium alloy product, the method including providing an alloy consisting essentially of, in wt. %:

Zn: 6 - 16  
Cu: 1 - 3  
30 Mg: 1.5 - 4.5,

one or more elements selected from Zr, Cr, Mn, Ti, V, or Hf, the total of said elements not exceeding 1.0 wt.%, the balance aluminium and incidental impurities. The aluminium alloy is solution heat-treated after casting, precipitation-hardened to increase its strength to a level exceeding the as-solution heat treated strength level by  
35 about 30% of the difference between as-solution heat-treated strength and peak-strength and thereafter subjected to a treatment at a sufficient temperature or

temperatures for improving its corrosion resistance properties. Thereafter, the alloy is again precipitation-hardened to raise its yield strength and produce a corrosion resistant alloy product. The ageing temperatures disclosed therein are between 170°C and 260°C in a range of 0.2 min. to 3 hours. The artificial ageing step is thereby  
5 preceded and succeeded by a precipitation-hardening step, also known as T77 ageing. Tensile strength values were obtained of between 460 MPa and 486 MPa and yield strength of 400 MPa to 434 MPa.

US Patent No. 5,035,754 discloses a heat-treating method for a high strength aluminium alloy comprising the steps of solution heat-treating an aluminium alloy  
10 consisting essentially of, in wt. %:

Zn: 3 - 9

Cu: 1 - 3

Mg: 1 - 6,

at least one element selected from the group consisting of

15 Cr: 0.1 - 0.5

Zr: 0.1 - 0.5

Mn: 0.2 - 1.0,

the balance being aluminium, heating of the alloy to a temperature of a lower temperature zone of 100°C to 140°C, optionally maintaining the alloy at a temperature  
20 within the lower temperature zone for a certain duration of time, re-heating the alloy to a temperature of an upper temperature zone of from 160°C to 200°C, optionally maintaining the alloy at a temperature within the upper temperature zone for a second duration of time, cooling of the alloy to a temperature of a lower temperature zone and repeating the above mentioned steps at least twice. Such alloy improves the  
25 properties of AA7075 and AA7050 aluminium alloys by obtaining a good corrosion resistance and a high strength characteristic. Some samples show a tensile strength of 57 to 62 kgf/mm<sup>2</sup> and values of the exfoliation rating of P or EA. The threshold stress value of the SCC-test was more than 50 kgf/mm<sup>2</sup>.

EP-0377779 discloses a process for producing an alloy for sheet or thin plate applications in the field of aerospace such as upper-wing members with high toughness and good corrosion properties which comprises the steps of working a body having a composition consisting of, in wt. %:

Zn: 7.6 - 8.4

Cu: 2.2 - 2.6

35 Mg: 1.8 - 2.1,

and one or more elements selected from

Zr: 0.5 - 0.2  
Mn: 0.05 - 0.4  
V: 0.03 - 0.2  
Hf: 0.03 - 0.5,

5 the total of said elements not exceeding 0.6 wt.%, the balance aluminium plus incidental impurities, solution heat treating and quenching said product and artificially ageing the product by either heating the product three times in a row to one or more temperatures from 79°C to 163°C or heating such product first to one or more temperatures from 79°C to 141°C for two hours or more or heating the product to one  
10 or more temperatures from 148°C to 174°C. These products show an improved exfoliation corrosion resistance of "EB" or better with about 15% greater yield strength than similar sized AA7x50 counter parts in the T76-temper condition. They still have at least about 5% greater strength than their similarly-sized AA7x50-T77 counter-part.

US Patent No. 5,312,498 discloses another method for producing an aluminium-  
15 based alloy product having improved exfoliation resistance and fracture toughness with balanced zinc, copper and magnesium levels such that there is no excess of copper and magnesium. The method of producing the aluminium-based alloy product utilizes either a one-step or two-step ageing process in conjunction with the stoichiometrically balancing of copper, magnesium and zinc. A two-step ageing  
20 sequence is disclosed wherein the alloy is first aged at about 121°C for about 9 hours followed by a second ageing step at about 157°C for about 10 to 16 hours followed by air cooling. Such ageing method is directed to thin plate or sheet products that are used for lower-wing skin applications or fuselage skin.

There is, however, a demand in the fields of aeronautics to provide high strength  
25 AA7000-series alloys with a cross-sectional thickness of more than 50 mm for e.g. spars or bars of wings and upper-wing skin applications with the above mentioned specific mechanical properties such as high strength, high toughness and good corrosion properties such as resistance to stress corrosion or resistance to exfoliation corrosion. These parts such as spars of wings for aircraft are typically manufactured  
30 from a plate product via machining operations wherein the material property is a compression yield strength in the L-direction at S/4 of at least 475 MPa, an ultimate tensile strength of at least 510 MPa and an ST (short transverse) elongation at S/2 of at least 3.0 %.

EP-1158068A1 discloses a heat-treatable aluminium alloy for producing thick  
35 products having a thickness of more than 12 mm, the alloy is an Al-Zn-Cu-Mg alloy with the following composition, in wt.%:

	Zn:	4 - 10
	Cu:	1 - 3.5
	Mg:	1 - 4
	Cr:	< 0.3
5	Zr:	< 0.3
	Si:	< 0.5
	Fe:	< 0.5

other elements < 0.05 each and < 0.15 in total, balance aluminium. It is disclosed that it was found that for thick products with an only slightly recrystallized microstructure, a high as-cast grain size could lead to a specific microstructure of the transformed and heat-treated product which has a beneficial effect on the toughness with no reduction in strength or other properties. It is therefore described to cast the alloy in the form of a rolling, forging or extrusion ingot such that the as-cast grain size is kept between 300 and 800  $\mu\text{m}$ .

It is therefore the object of the present invention to provide an improved method for producing a high strength Al-Zn-Cu-Mg alloy for thick plate products with an improved fatigue crack growth resistance and a high damage tolerance which has the aforementioned properties of a compression yield strength (in L-direction at S/4) of at least 475 MPa, an ultimate tensile strength of at least 510 MPa and an ST elongation at S/2 of at least 3.0 %.

It is another object of the invention to obtain an AA7000-series aluminium alloy which exhibits strength in the range of T6-type tempers and toughness and corrosion resistance properties in the range of T73-type tempers.

It is furthermore an object of the present invention to obtain a thick plate alloy, which can be used to produce structural parts of aircraft such as spars of wings with high strength levels and good corrosion resistance properties.

The present invention meets these objects by the characterizing features of claim 1. Further preferred embodiments are described and specified within the sub-claims.

According to the invention there is disclosed a method for producing a high strength Al-Zn-Cu-Mg alloy with an improved fatigue crack growth resistance and a high damage tolerance, comprising the steps of:

a) casting an ingot with the following composition (in weight percent):

	Zn:	5.5 - 9.5
35	Cu:	1.5 - 3.5

- Mg: 1.5 - 3.5  
Mn: < 0.25  
Zr: < 0.25, preferably 0.06 - 0.16  
Cr: < 0.10  
5 Fe: < 0.25, preferably < 0.15  
Si: < 0.25, preferably < 0.10  
Ti: < 0.10  
Hf and/or V < 0.25, and  
other elements each less than 0.05 and less than 0.15 in total, balance  
10 aluminium,  
b) homogenising and/or pre-heating the ingot after casting,  
c) hot working the ingot, preferably by means of rolling, and optionally cold  
working, preferably by means of rolling, into a worked product of more than 50  
mm thickness,  
15 d) solution heat treating,  
e) quenching the solution heat treated product, and artificially ageing the worked  
and heat-treated product, wherein the ageing step comprises a first heat treatment at  
a temperature in a range of 105°C to 135°C for more than 2 hours and less than 8  
hours and a second heat treatment at a higher temperature than 135°C but below  
20 170°C for more than 5 hours and less than 15 hours to achieve a product with a  
compression yield strength in L-direction at S/4 of at least 475 MPa, an ultimate tensile  
strength of at least 510 MPa and an ST elongation at S/2 of at least 3.0%.

The above mentioned combination of chemistry and ageing practice exhibit very  
high strength levels, very good exfoliation resistance and high stress corrosion  
25 resistance for thick plate products with thickness of more than 50 mm. Specifically, the  
two-step ageing practice of the present invention utilizes a first heat treatment for 2 to  
5 hours, at temperatures in the range of 115°C to 125°C, preferably about 4 hours at  
120°C and a second heat treatment for 5 to 15 hours, at temperatures in the range of  
155°C to 169°C, preferably for about 13 hours at temperatures between 161°C to  
30 167°C.

It will be immediately apparent to the skilled person that in the method according  
to this invention, that after quenching of the solution heat treated product and before  
the artificial ageing practice, the product may optionally be stretched or compressed or  
otherwise cold worked to relieve stresses as known in the art.

35 Preferred amounts (in wt.%) of magnesium are in a range of 1.5 to 2.5,  
preferably in a range of 1.6 to 2.3, and more preferably in the range of 1.90 to 2.10.



Preferred amounts (in wt.%) of copper are in a range of 1.5 to 2.5, preferably in a range of 1.6 to 2.3, and more preferably in the range of 1.85 to 2.10. Preferred amounts (in wt.%) of zinc are in a range of 5.9 to 6.2 or in a range of 6.8 to 7.1 or in a range of 7.8 to 8.1.

5       Copper and magnesium are important elements for adding amongst others strength to the alloy. The preferred range of copper and magnesium is above 1.6 wt.% and lower than 2.3 wt.% since too low amounts of magnesium and copper result in a decrease of strength while too high amounts of magnesium and copper result in a lower corrosion performance and problems with the weldability of the alloy product. In  
10       order to achieve a compromise in strength, toughness and corrosion performance each of copper and magnesium amounts (in weight %) of between 1.6 and 2.3, with preferred narrower ranges set out above and in the claims, have been found to give a good balance for thick alloy products. If the amounts of copper and magnesium are chosen too high the properties relating to toughness, stress corrosion and elongation  
15       will drop, especially for thicker products.

      Furthermore, it has been found that the balance of copper and magnesium to zinc, especially the balance of magnesium to zinc is of importance. Depending on the amount of zinc the amount (in wt.%) of magnesium is preferably in between 2.4-0.1[Zn] and 1.5+0.1[Zn]. That means that the amount of magnesium depends on the  
20       chosen amount of zinc. With an amount of approx. 6 wt.% Zn the amount (in wt.%) of magnesium is between 1.8 and 2.1, when Zn is approx. 7 % the amount of magnesium is between 1.7 and 2.2 and if Zn is approx. 8 % the amount of magnesium is between 1.6 and 2.3.

      With the method according to the present invention and the chosen balance of  
25       copper, magnesium and zinc it is possible to obtain a homogenised and/or pre-heated ingot after casting which is hot-worked and optionally cold-worked into a worked product of preferably more than 60 mm thickness, more preferably in a range of 110 mm to 160 mm and even up to 220 mm thickness with an improved corrosion performance which is at least as good as achievable with the T77 ageing method but  
30       less complicated than the so-called three-step-ageing temper T77.

      The alloy of the present invention is preferably selected from the group consisting of AA7010, AA7x50, AA7040, AA7020, AA7x75, AA7349 or AA7x55 or AA7x85, preferably AA7055, AA7085.

      According to the invention there is disclosed a plate product of high strength  
35       aluminium-zinc-copper-magnesium-alloy produced in accordance with a method as defined above having a thickness of more than 50 mm, preferably 100 mm to 220 mm.

Such plate product is preferably a part of an aircraft such as a bar or a spar of a wing. Most preferably, the plate product according to the present invention is an upper-wing member of an aircraft.

#### EXAMPLES

5 The foregoing and other features and advantages of the alloys according to the invention will become readily apparent from the following detailed description of preferred embodiments.

On an industrial scale 7 different aluminium alloys have been cast into ingots having the following chemical composition as set out in Table 1.

10

**Table 1.** Chemical composition of thick plate alloys, in wt.%, balance aluminium and inevitable impurities, Fe = 0.08 and Si = 0.04, and Zr = 0.10, Alloys 1 to 5 with Mn = 0.02 and Alloys 6 and 7 with Mn = 0.08.

Alloy	Alloying Element			
	Cu	Mg	Zn	Zr
1	2.16	2.04	6.18	0.11
2	2.10	2.00	6.10	0.10
3	2.14	2.04	6.12	0.10
4	1.91	2.13	6.86	0.11
5	2.20	2.30	6.90	0.10
6	2.23	2.50	7.80	0.10
7	1.82	2.18	8.04	0.10

15 Full scale ingots have been sawn from the ingot slices, homogenised for 12 hours at 470°C and for 24 hours at 475°C, pre-heated for 5 hours at 410°C and hot-rolled to a thickness of various gauges as identified in Table 2. Thereafter, the plates were solution heat treated for 4 hours at 475°C with subsequent quenching and a two-step ageing process, first for 4 hours at 120°C and second for 13 hours at 165°C.

20 The alloys mentioned in Table 1 were examined with regard to various plate thickness as identified in Table 2.

**Table 2.** Overview of strength, elongation and exfoliation properties of different thickness of the alloys of Table 1 (S/2 = mid-thickness; S/4 = quarter-thickness); EXCO testing at S/10 according to ASTM G34, samples shown for EA-ED classification.

25

Plate thickness (mm)	Alloy	Rp-L (MPa) S/4	Rm-L (MPa) S/4	A-(ST) (%) S/2	EXCO
63.5	1	553	590	6	EC
110	2	503	553	4	EA
152	3	495	537	5	EA
152	3*	480	528	5	EA
63.5	4	570	604	3	EC
110	5	515	550	2	EA
110	6	510	565	2	EA
152	7	476	529	3	EA

\* aged at 120° for 5 hours and subsequently at 165°C at 15 hours.

As shown in Table 2 the alloys of Table 1 show good compression yield strength ("Rp") in the L-direction of more than 476 MPa, most of them more than 500 MPa while the ultimate tensile strength ("Rm") in the L-direction is above 529 MPa for all alloys and thickness, one example even above 600 MPa for 63.5 mm. The ST-elongation at position S/2 of all but two alloys is 3 % or above, even up to 6 %.

The exfoliation properties are EA or EC. The exfoliation testing was done in accordance to ASTM G34 at S/10 position. The exfoliation properties are similar for similar ageing steps as shown in Table 3 but surprisingly deteriorate if the first heat treatment is longer and the second heat treatment is shorter.

**Table 3.** Exfoliation properties ("EXCO") of selected alloys of Table 1 according to ASTM G34 ("-" means not measured).

Alloy	Thickness	6h/120°C + 6h/155°C	5h/120°C + 12h/155°C	4h/120°C + 13h/165°C
1	63.5	EC	-	EC
3	110	-	EA	EA
5	63.5	EC	-	-
5	110	EC	EA	EA
6	110	ED	EA	EA
7	63.5	EC	-	EA

Alloy 4 has been tested with a plate thickness of 110 mm. The results of toughness and elongation are shown in Table 4.

**Table 4.** Toughness and elongation properties of selected alloys of Table 1, all plates of 110 mm thickness, ageing according to a two-step method, first heat treatment at 120°C for 4 hours, second heat treatment at 165°C for 13 hours, alloy 5 with a copper content of 2.25;  $K_{IC}$  measured according to norm ASTM E399-90 C(T) specimens, thickness of 38.1mm (1.5") for SL, SL samples taken from mid-thickness (S/2).

Alloy	R <sub>p</sub> (S/2, ST)	A (S/2, ST)	K <sub>IC</sub> (S/2, SL)
1	465	5	26.9
3	461	5	26.8
4	465	5	27.1
5	453	2	24.1
6	472	1	19.5
7	482	3	26.4

All above mentioned alloys showed an exfoliation rating of EA for the selected plate thickness of 110 mm.

Finally, the stress corrosion properties ("SCC") were examined. First, alloys 1 and 4 were tested with thickness of 152 mm. Two different ageing procedures were selected in accordance with Table 5. The load level was 172 MPa. The test direction is S-L. Samples were taken from the S/2 position. Table 5 shows the number of days till failure was given. After 30 days the test was terminated. "NF" means no failure after 30 days, "30" means failure after 30 days. In total at least three specimens are tested per variant. The test was done in accordance with ASTM G47.

**Table 5.** SCC-properties for thickness of 152 mm for two alloys.

Alloy	5h/120°C + 12h/165°C	4h/120°C+15h/165°C
1	NF, NF, NF	NF, NF, NF
4	30, NF, NF	NF, NF, NF

Finally, 5 other alloys were tested with regard to the stress corrosion properties by using plates of a thickness of 125 mm. Samples were taken from the S-L direction at a load level of 180 MPa. Table 6 shows the chemistry and the results of those alloys with regard to the stress corrosion properties.

**Table 6.** SCC-properties of S-L specimens having a thickness of 125 mm, Fe = 0.08, Si = 0.04, and Zr = 0.10.

Alloy	Cu	Mg	Zn	4h/120°C+13h/165°C
A	1.7	1.8	7.4	NF, NF, NF
B	2.3	1.8	7.5	NF, NF, NF
C	2.25	2.5	7.65	15, NF, NF
D	1.8	2.45	8.0	15, 20, NF
E	2.3	2.4	8.1	20, 25, NF

5 As can be seen from Table 6 the toughness of the inventive alloy is controlled by the copper and magnesium levels while zinc has an influence in particular on the tensile properties. The preferred balance of each of copper and magnesium is in between 1.6 and 2.0 wt.%.

10 Having now fully described the invention, it will be apparent to one of ordinary skill in the art that many changes and modifications can be made without departing from the scope of the invention as herein described.

**CLAIMS**

1. Method for producing a high strength Al-Zn-Cu-Mg alloy with a high damage tolerance and an improved corrosion resistance, comprising the steps of:
- 5 a) casting an ingot with the following composition (in weight percent):
- |                |                                 |
|----------------|---------------------------------|
| Zn             | 5.5 to 9.5                      |
| Cu             | 1.5 to 3.5                      |
| Mg             | 1.5 to 3.5                      |
| Mn             | < 0.25                          |
| 10 Zr          | < 0.25, preferably 0.06 to 0.16 |
| Cr             | < 0.10                          |
| Fe             | < 0.25                          |
| Si             | < 0.25                          |
| Ti             | < 0.10                          |
| 15 Hf and/or V | < 0.25                          |
- other elements each less than 0.05 and less than 0.15 in total, balance aluminium,
- b) homogenising and/or pre-heating the ingot after casting,
- c) hot-working the ingot and optionally cold working into a worked product of
- 20 more than 50 mm thickness,
- d) solution heat treating,
- e) quenching the solution heat treated product, and
- f) artificially ageing the worked and heat-treated product, wherein the ageing
- 25 step comprises a first heat treatment at a temperature in a range of 105°C to 135°C for more than 2 hours and less than 8 hours and a second heat treatment at a higher temperature than 135°C but below 170°C for more than 5 hours and less than 15 hours to achieve a product with a compression yield strength in L-direction at S/4 of at least 475 MPa, an ultimate tensile strength of at least 510 MPa and an ST elongation at S/2
- 30 of at least 3.0%.
2. Method according to claim 1, wherein the ageing step consists of two heat treatments, the first heat treatment is performed for 2 to 5 hours at temperatures in the range of 105°C to 135°C, and the second heat treatment is performed for
- 35 5 to 15 hours at temperatures in the range of 155°C to 169°C.

3. Method according to claim 1 or 2, wherein the first heat treatment is performed at temperatures in the range 115°C to 125°C.
- 5 4. Method according to any one of claims 1 to 3, wherein the first heat treatment is performed for 2 to 5 hours at about 120°C.
5. Method according to any one of claims 1 to 4, wherein the second heat treatment is performed at temperatures in the range 161°C to 167°C.
- 10 6. Method according to any one of claim 1 to 5, wherein the second heat treatment is performed for about 13 hours.
7. Method according to any one of claims 1 or 6, wherein the improved corrosion resistance has exfoliation properties ("EXCO") of EB or better according to ASTM G34.
- 15 8. Method according to any one of the preceding claims, wherein in the amount of Mg is in a range of 1.5 to 2.5, preferably in a range of 1.6 to 2.3, and more preferably in a range of 1.90 to 2.10.
- 20 9. Method according to any of the preceding claims, wherein the amount of Cu is in a range of 1.5 to 2.5, preferably in a range of 1.6 to 2.3, and more preferably in a range of 1.85 to 2.10.
- 25 10. Method according to any one of the preceding claims, wherein the amount of Mg depends on the amount of Zn as follows: [Mg] is in between  $2.4-0.1[\text{Zn}]$  and  $1.5+0.1[\text{Zn}]$ .
- 30 11. Method according to any one of the preceding claims, wherein the amount of Zn is in a range of 5.9 to 6.2, or in a range of 6.8 to 7.1, or in a range of 7.8 to 8.1.
- 35 12. Method according to any one of the preceding claims, wherein said high strength Al-Zn-Cu-Mg alloy is selected from the group of AA7010, AA7x50, AA7040, AA7020, AA7x75, AA7349, AA7x55, AA7x85.

13. Method according to any one of the preceding claims, wherein after homogenising and/or pre-heating the ingot after casting, hot working the ingot and optionally cold working into a worked product of 60 to 220 mm, and whereby the working is preferably carried out by means of rolling.
14. Method according to claim 13, wherein after homogenising and/or pre-heating the ingot after casting, hot working the ingot and optionally cold working into a worked product of 60 to 160 mm, and more preferably of 110 to 160 mm.
15. A plate product of high strength Al-Zn-Cu-Mg alloy produced in accordance with a method as defined in any one of the claims 1 to 14 and having a thickness of more than 50 mm, and preferably more than 60 mm.
16. A plate product according to claim 15, wherein said plate product is a structural member of an aircraft.
17. A plate product according to claim 15, wherein said plate product is a bar or a spar of a wing of an aircraft.
18. A plate product according to claim 15, wherein said plate product is an upper-wing member of an aircraft.
19. An aircraft structural member produced from a high strength Al-Zn-Cu-Mg alloy produced in accordance with a method as defined in one of the claims 1 to 14.
20. An aircraft structural member having a thickness of at least 50 mm, and preferably in a range of 50 to 160 mm, manufactured from a rolled product made of an alloy with a composition, consisting of, in % by weight:
- |    |                                 |
|----|---------------------------------|
| Zn | 5.5 to 9.5                      |
| Cu | 1.5 to 3.5                      |
| Mg | 1.5 to 3.5                      |
| Mn | < 0.25                          |
| Zr | < 0.25, preferably 0.06 to 0.16 |
| Cr | < 0.10                          |
| Fe | < 0.25                          |



Si < 0.25

Ti < 0.10

Hf and/or V < 0.25

other elements each less than 0.05 and less than 0.15 in total, balance  
aluminium,

and treated by solution heat treating, quenching, and ageing practice consisting  
of a first heat treatment at a temperature in a range of 105°C to 135°C for more  
than 2 hours and less than 8 hours and a second heat treatment at a higher  
temperature than 135°C but below 170°C for more than 5 hours and less than  
15 hours, the product having a compression yield strength in L-direction at S/4 of  
at least 475 MPa, an ultimate tensile strength of at least 510 MPa and an ST  
elongation at S/2 of at least 3.0%.

21. An aircraft structural member according to claim 20, wherein the improved  
corrosion resistance has exfoliation properties ("EXCO") of EB or better  
according to ASTM G34.

22. An aircraft structural member according to claim 20, forming a part of an aircraft  
upper wing.

23. An aircraft structural member according to claim 20, forming a spar or bar of an  
aircraft wing.

## INTERNATIONAL SEARCH REPORT

International Application No. .

PCT/EP 03/06208

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C22C21/10

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 315 842 B1 (VERDIER JEAN-FRANCOIS ET AL) 13 November 2001 (2001-11-13) column 1, line 21 - line 27 column 3, line 38 - line 67 column 5, line 7 - line 57 column 5, line 62 - column 11, line 22; examples 1-6 ---	1-23
A	US 3 881 966 A (STALEY JAMES T ET AL) 6 May 1975 (1975-05-06) column 1, line 12 - line 20 column 3, line 57 - column 7, line 2; examples 1C, 2E, 3E-M, 4; tables I-IV column 7, line 35 - line 42; example 6 --- -/-	1-23

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

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- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

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- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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- \* & \* document member of the same patent family

Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/06208

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 196 021 A (BOUVAIST JEAN ET AL) 1 April 1980 (1980-04-01) column 5, line 55 -column 6, line 11; example IV -----	1-23
A	US 5 863 359 A (KARABIN LYNETTE M ET AL) 26 January 1999 (1999-01-26) column 4, line 59 -column 5, line 6 claims 12,29 -----	1-23
A	EP 0 514 292 A (PECHINEY RHENALU) 19 November 1992 (1992-11-19) the whole document -----	15

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/EP 03/06208

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 6315842	B1	13-11-2001	NONE	
US 3881966	A	06-05-1975	NONE	
US 4196021	A	01-04-1980	FR 2393070 A1	29-12-1978
			AU 519309 B2	26-11-1981
			AU 3677078 A	06-12-1979
			BE 867709 A1	01-12-1978
			CA 1125547 A1	15-06-1982
			CH 634354 A5	31-01-1983
			DE 2824136 A1	14-12-1978
			ES 470318 A1	01-01-1979
			GB 1603690 A	25-11-1981
			IL 54818 A	23-02-1983
			IT 1095276 B	10-08-1985
			JP 1380500 C	28-05-1987
			JP 54002216 A	09-01-1979
			JP 56013784 B	31-03-1981
			NL 7806060 A	05-12-1978
			SE 426712 B	07-02-1983
			SE 7806251 A	03-12-1978
			US 4659393 A	21-04-1987
			ZA 7803147 A	25-07-1979
US 5863359	A	26-01-1999	US 5865914 A	02-02-1999
EP 0514292	A	19-11-1992	FR 2676462 A1	20-11-1992
			CA 2068597 A1	15-11-1992
			DE 69212533 D1	05-09-1996
			DE 69212533 T2	28-11-1996
			EP 0514292 A1	19-11-1992